

AD-A102 112

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/6 7/3
PHOTOCHEMISTRY OF SURFACE-CONFINED ORGANOMETALLICS: PHOTOCHEMIC--ETC(U)
JUN 81 C L REICHEL, M S WRIGHTON N00014-75-C-0880

UNCLASSIFIED

TR-28

NL

[OF]
AD-A
102 112

END
DATE
FILMED
8-81
DTIC

UNCLASSIFIED

LEVEL II

12

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-28	2. GOVT ACCESSION NO. AD-A202 112	3. RECIPIENT CATALOG NUMBER
4. TITLE (and Subtitle) Photochemistry of Surface-Confined Organo-metallics: Photochemical Release of a Surface-Confined Cobalt Carbonyl Catalyst		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
6. AUTHOR(s) Carol L. Reichel and Mark S. Wrighton		7. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0880		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Rm. 6-335 Massachusetts Institute of Technology Cambridge, Massachusetts 02139		10. PROGRAM ELEMENT PROJECT TASK AREA & WORK UNIT NUMBERS NR 051-579
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE June 8, 1981
		13. NUMBER OF PAGES 48
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 118 21 1250		15. SECURITY CLASS. (of this report) UNCLASSIFIED
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States Government; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared and accepted for publication in the Journal of the American Chemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Surface-confined catalysis, organometallic photocatalysis, photochemistry, derivatized surfaces.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Inorganic oxide surfaces, SiO_2 and Al_2O_3 , bearing $-\text{OH}$ functionality have been functionalized with $-\text{Co}(\text{CO})_2$ by first treating the solids with $(\text{EtO})_3\text{SiH}$, Me_2ClSiH or Cl_3SiH to introduce $-\text{SiH}$ functionality followed by reaction with $\text{Co}_2(\text{CO})_8$. Derivatized surfaces have been characterized by infrared spectroscopy and compared to solution analogues to confirm the presence of $-\text{SiH}$ and		

DD FORM 1473

JAN 73

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-014-66011

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A102112

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

$\rightarrow \text{SiCo}(\text{CO})_4$ groups on the surface. The surface-confined $\rightarrow \text{SiCo}(\text{CO})_4$ undergoes photoreactions that begin with loss of CO subsequent to optical excitation in the near-ultraviolet. The photochemistry closely parallels the behavior of solution $\text{R}_3\text{SiCo}(\text{CO})_4$ analogues; CO can be photosubstituted by $\text{P}(\text{OPh})_3$ and the surface-confined $\rightarrow \text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ species is detectable by infrared spectroscopy. Irradiation of the oxide powders bearing $\rightarrow \text{SiCo}(\text{CO})_4$ suspended in Et_3SiH solutions results in the release of the $\rightarrow \text{Co}(\text{CO})_4$ into solution as $\text{Et}_3\text{SiCo}(\text{CO})_4$ concurrent with the regeneration of surface $\rightarrow \text{SiH}$ functionality. Irradiation of the powders ($\rightarrow \text{SiCo}(\text{CO})_4$) in the presence of 1-pentene yields $\text{Co}(\text{CO})_4$ in solution and surface $\rightarrow \text{Si}(\text{pentenyl})$ groups. In the presence of Et_3SiH /1-pentene photoactivated catalysis by the derivatized powders ($\rightarrow \text{SiCo}(\text{CO})_4$) occurs to give isomerization of the alkene, hydrosilation to give $\text{Et}_3\text{Si}(\text{n-pentyl})$, and small amounts of n-pentane. Reaction under H_2 improves the relative yield of n-pentane while H_2/CO mixtures yield no hydroformylation products and lower the observed rate due to CO competing for the coordinatively unsaturated species. The surface $\rightarrow \text{SiH}$ groups also add to 1-pentene to give powders bearing $\rightarrow \text{Si}(\text{n-pentyl})$ functionality. The use of powders functionalized with $\rightarrow \text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ also gives catalysis upon photoexcitation, but the product distribution differs significantly and includes at least two isomers of $\text{Et}_3\text{Si}(\text{pentenyl})$. In all cases the bulk of the catalysis appears to result from Co-carbonyl fragments photoreleased from the oxide support. The initial rate of catalysis appears to depend on the initial rate at which the fragments are released into homogeneous solution. The heterogeneous photocatalysts thus give the same product distribution as appropriate homogeneous precursors, but the oxide supported $\rightarrow \text{SiCo}(\text{CO})_4$ is more easily isolated and handled and more durable than $\text{R}_3\text{SiCo}(\text{CO})_4$.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-75-C-0880

Task No. NR 051-579

TECHNICAL REPORT NO. 28

"PHOTOCHEMISTRY OF SURFACE-CONFINED ORGANOMETALLICS: PHOTOCHEMICAL
RELEASE OF A SURFACE-CONFINED COBALT CARBONYL CATALYST"

by

Carol L. Reichel and Mark S. Wrighton

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for publication in the Journal of the American Chemical Society

June 8, 1981

Reproduction in whole or in part is permitted for any
purpose of the United States Government

This document has been approved for public release and
sale; its distribution is unlimited.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

Photochemistry of Surface-Confined Organometallics: Photochemical
Release of a Surface-Confined Cobalt Carbonyl Catalyst[†]

Carol L. Reichel and Mark S. Wrighton^{*}

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

[†]This paper is dedicated to George S. Hammond in honor of his 60th birthday.

Abstract: Inorganic oxide surfaces, SiO_2 and Al_2O_3 , bearing $-\text{OH}$ functionality have been functionalized with $-\text{Co}(\text{CO})_4$ by first treating the solids with $(\text{EtO})_3\text{SiH}$, Me_2ClSiH , or Cl_3SiH to introduce SiH functionality followed by reaction with $\text{Co}_2(\text{CO})_8$. Derivatized surfaces have been characterized by infrared spectroscopy and compared to solution analogues to confirm the presence of SiH and $\text{SiCo}(\text{CO})_4$ groups on the surface. The surface-confined $\text{SiCo}(\text{CO})_4$ undergoes photoreactions that begin with loss of CO subsequent to optical excitation in the near-ultraviolet. The photochemistry closely parallels the behavior of solution $\text{R}_3\text{SiCo}(\text{CO})_4$ analogues; CO can be photosubstituted by $\text{P}(\text{OPh})_3$ and the surface-confined $\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ species is detectable by infrared spectroscopy. Irradiation of the oxide powders bearing $\text{SiCo}(\text{CO})_4$ suspended in Et_3SiH solutions results in the release of the $-\text{Co}(\text{CO})_4$ into solution as $\text{Et}_3\text{SiCo}(\text{CO})_4$ concurrent with the regeneration of surface SiH functionality. Irradiation of the powders ($\text{SiCo}(\text{CO})_4$) in the presence of 1-pentene yields $\text{Co}_4(\text{CO})_{12}$ in solution and surface $\text{Si}(\text{pentenyl})$ groups. In the presence of Et_3SiH /1-pentene photoactivated catalysis by the derivatized powders ($\text{SiCo}(\text{CO})_4$) occurs to give isomerization of the alkene, hydrosilation to give $\text{Et}_3\text{Si}(\text{n-pentyl})$, and small amounts of n-pentane. Reaction under H_2 improves the relative yield of n-pentane, while H_2/CO mixtures yield no hydroformylation products and lower the observed rate due to CO competing for the coordinatively unsaturated species. The surface SiH groups also add to 1-pentene to give powders bearing $\text{Si}(\text{n-pentyl})$ functionality. The use of powders functionalized with $\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ also gives catalysis upon photoexcitation, but the product distribution differs significantly and includes at least two isomers of $\text{Et}_3\text{Si}(\text{pentenyl})$. In all cases the bulk of the catalysis appears to result from Co-carbonyl fragments photoreleased from the oxide support. The initial rate of catalysis appears to depend on the initial rate at which the fragments are released into homogeneous solution. The heterogeneous photocatalysts thus give the same product distribution as appropriate homogeneous precursors, but the oxide supported $\text{SiCo}(\text{CO})_4$ is more easily isolated and handled and more durable than $\text{R}_3\text{SiCo}(\text{CO})_4$.

Chemistry of surfaces modified with molecular reagents may have use in stoichiometric and catalytic syntheses, in adhesion and other surface physical tailoring, in analysis and separations, and in chemical energy conversion.¹⁻¹⁰ Successful application of molecular modification depends on characterization of both the structure and reactivity of the surface-confined species. One aim of research in this laboratory has been to initiate catalysis by optical excitation of thermally inert, surface-confined organometallic reagents. Thermally inert, surface-confined $-\text{Fe}(\text{CO})_n$ reagents have been demonstrated to be photochemical precursors to catalysts for olefin isomerization and hydrosilation.¹¹ The anchoring surface for the $-\text{Fe}(\text{CO})_n$ was a phosphinated polystyrene polymer, $\text{(P)}-$, where the organic polymer can be regarded as an insoluble, though solvent swellable, triarylphosphine ligand. For the $\text{(P)}-\text{Fe}(\text{CO})_n$ system we found that the Fe-P anchor bond is sufficiently photoinert that olefin isomerization could be concluded to occur when the Fe-P bond is still intact. However, the polymer appeared to be sufficiently flexible that photogenerated coordinative unsaturation does not persist for extended periods. Further, it is likely that the $\text{(P)}-$ system would be reactive to extensively coordinatively unsaturated $\text{Fe}(0)$ species. Consequently, we have now turned attention to inorganic oxides as surfaces to which photochemical catalyst precursors can be attached. Inorganic oxides such as SiO_2 and Al_2O_3 should be inert, can be functionalized, and are transparent to ultraviolet and visible light over a wider range than for the $\text{(P)}-$ system.

The system described in this article is the surface-confined >SiCo(CO)_4 , $\text{(S)}-\text{SiCo(CO)}_4$, where the $\text{(S)}-$ is Al_2O_3 or SiO_2 . The photochemistry and photocatalytic activity of $\text{R}_3\text{SiCo(CO)}_4$ ($\text{R} = \text{Et}, \text{Ph}$) have recently been described.¹² The $\text{(S)}-\text{SiCo(CO)}_4$ materials are air stable at 25°C for

prolonged periods in contrast to $\text{Et}_3\text{SiCo(CO)}_4$, but the (S)-SiCo(CO)_4 is very photosensitive. The photoactivity can be used to release catalytically active species into solution, but the primary photoprocess is CO release, not Co-Si bond cleavage. A preliminary communication has established that photochemical Si-Co bond cleavage does not occur; irradiation under ^{13}CO yields $\text{(S)-SiCo(CO)}_n(^{13}\text{CO})_{4-n}$, not the release of Co(CO)_4 to form $\text{Co}_2(\text{CO})_n(^{13}\text{CO})_{8-n}$.¹³

Studies of the surfaces of insulating metal oxides are not easily probed by surface sensitive electron spectroscopies. We have made use of Fourier transform transmission infrared to characterize the surfaces functionalized with ≡SiH and ≡SiCo(CO)_4 . This technique affords a molecular specific probe of structure and allows monitoring of the dilute catalytic sites of interest. As shown below, the surfaces of Al_2O_3 and SiO_2 that we have used for photocatalysis have many surface functionalities present. As in solution, we exploit the fact that a chromophore, ≡SiCo(CO)_4 , present in dilute amounts can be selectively activated by light. This represents one of the major advantages for optical vs. thermal activation of catalysis; in principle, the activation energy can be deposited selectively into the sites that are active.

Experimental

Physical Measurements and Analysis. Infrared spectra of surfaces were taken as KBr pellets (~10% Al_2O_3 or SiO_2) on a Perkin-Elmer Model 180 dispersion or a Nicolet 7199 Fourier transform spectrometer. Solutions were analyzed in matched 1.0 mm or 0.1 mm pathlength sealed NaCl cells. Electronic spectra of solutions were obtained on a Cary 17 uv-vis-nir spectrophotometer in 1.00 cm quartz or 100 cm Pyrex cells. Gas chromatographic analyses were performed on a Varian Model 1440 or 2440 gas chromatograph equipped with flame ionization detectors and interfaced with a Hewlett-Packard model 3370S recording integrator. Hydrocarbon products were analyzed at 20°C on columns of 20% propylene carbonate on Chromosorb P (Johns-Manville, 1/8" x 30') against internal standard, n-hexane. Hydrosilation products were analyzed at 60°C on columns of 20% 3,3'-oxydipropionitrile (Applied Science Laboratories, 1/8" x 30') against an internal standard, n-decane. Authentic samples of all products were available for calibration of the detector response and for retention time comparisons.

Reaction Conditions. All manipulations of O_2 - and H_2O -sensitive materials were performed in a Vacuum Atmospheres He-43-6 Dri-Lab glove box with an attached HE-493 Dri-Train or in conventional Schlenk glassware under an N_2 atmosphere. Samples for irradiation were freeze-pump-thaw degassed at least 4 times in 13 mm o.d. Pyrex ampules containing 2 mm x 7 mm Teflon-coated magnetic stirring bars, and sealed hermetically under vacuum (10^{-5} torr). Reactions under H_2 were performed in 13 mm o.d. Pyrex tubes fused to ground-glass joints, which were connected to a source of vacuum and of H_2 . The system was flushed at least 4 times with H_2 before H_2 gas was admitted to the sample under vacuum. Irradiations were performed with a medium-pressure Hg arc lamp (Hanovia, 450 W) fitted with a supplementary H_2O filter to remove infrared radiation; or at lower intensities with 2 General Electric #F15T8/BLB

Black Lites ($\lambda_{\text{max}} = 355 \pm 20 \text{ nm}$; $\sim 2 \times 10^{-6} \text{ ein/min}$ as determined by ferrioxalate actinometry).¹⁴

Materials. Chromatographic grade $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (Davison Chemical Company, 80-200 mesh) was used as received. Chromatographic grade natural Al_2O_3 (Voelm grade I) was activated for 24 hr at 450°C before use and stored in the dry box. High surface area $\gamma\text{-Al}_2\text{O}_3$ ($200 \text{ m}^2/\text{g}$, Strem) was received as pellets and used as received or pulverized before use in some experiments. Powdered, high surface area SiO_2 ($400 \text{ m}^2/\text{g}$, Alfa) was used as received. 1-pentene (99%, Phillips Chemical Company) and HSiEt_3 (Petrarch) were passed through activated Al_2O_3 prior to use and stored in amber bottles at 4°C . Triphenylsilane (Petrarch) was recrystallized from *n*-pentane prior to use. Triethoxysilane (Petrarch) was freeze-pump-thaw degassed upon receipt and stored in the dry box. $\text{Co}_2(\text{CO})_8$ (Strem), *n*-hexane (Aldrich), *n*-decane (Aldrich), HSiCl_3 (Aldrich), and $\text{Me}_2\text{C}^*\text{SiH}$ (Petrarch) were used as received. $\text{R}_3\text{SiCo}(\text{CO})_4$ ($\text{R} = \text{Et}, \text{Ph}$) were prepared as previously described and stored at 0°C under N_2 .¹² $\text{Co}_4(\text{CO})_{12}$ was prepared by heating $\text{Co}_2(\text{CO})_8$ in isooctane at $80\text{--}90^\circ\text{C}$ for 12 hr. The product was filtered off, recrystallized from benzene/isooctane and stored at 0°C under N_2 . Hydrocarbon solvents were distilled from CaH_2 under N_2 ; THF was distilled from Na/benzophenone under N_2 .

Derivatization of Oxide Supports. A typical procedure is outlined. 1.6 ml $\text{HSi}(\text{OEt})_3$ in 10 ml isooctane under N_2 was added to 4 g of powdered Al_2O_3 in a Schlenk tube. In some cases, 0.12 ml distilled H_2O was added via syringe. The suspension was allowed to stand at 25°C under slow N_2 purge for 12-36 hr with periodic agitation, after which time excess solution was drained off. In some cases, the >SiH derivatized surface was washed with hexanes and isolated at this stage. Under N_2 , a solution of 1.4 g $\text{Co}_2(\text{CO})_8$ in 10 ml isooctane was added by syringe. After 12 hr at 25°C under slow N_2 purge with intermittent agitation, the tube was opened in the dark. The derivatized powder was washed with a copious quantity of hexanes or pentane until the rinsings were colorless. The derivatized powder was dried under vacuum at 25°C .

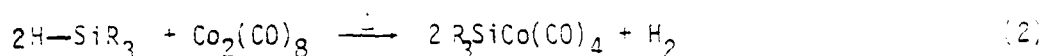
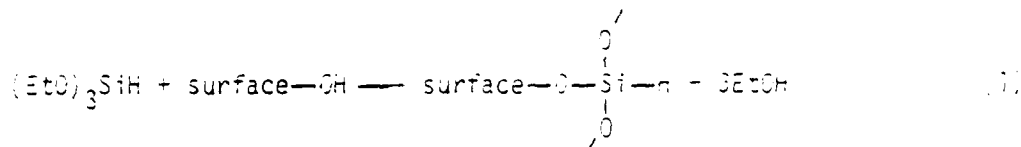
Functionalization using Me_2ClSiH was carried out in a manner similar to that for Cl_3SiH or $(\text{EtO})_3\text{SiH}$ except that dry Et_3N was added. A typical procedure was to react 2 g of Al_2O_3 or SiO_2 with 5 ml Me_2ClSiH and 4 ml of Et_3N in 50 ml of isooctane for 24 h at 20°C . The excess Me_2ClSiH , Et_3N , and isooctane were stripped off under vacuum. The solid was washed with isooctane leaving the $(\text{S})-\text{SiMe}_2\text{H}$ and the $\text{Et}_3\text{N}\cdot\text{HCl}$. The $\text{Et}_3\text{N}\cdot\text{HCl}$ was removed by washing with CH_2Cl_2 and again with isooctane. To further functionalize to form $(\text{S})-\text{SiMe}_2\text{Co}(\text{CO})_4$ the $(\text{S})-\text{SiMe}_2\text{H}$ was reacted with excess $\text{Co}_2(\text{CO})_8$ in isooctane under N_2 for 22 h at 20°C . The solid was washed with isooctane and dried under vacuum.

The surface >SiH and $\text{>SiCo}(\text{CO})_4$ are infrared detectable, Table I. Typical analyses were performed by making measurements of KBr pellets containing $(\text{S})-\text{SiH}$ and/or $(\text{S})-\text{SiCo}(\text{CO})_4$ (~10% by weight). The pellets are made in as reproducible a fashion as possible. 200 mg of dry, infrared grade KBr and 20 mg of $(\text{S})-\text{SiH}$ or $(\text{S})-\text{SiCo}(\text{CO})_4$ are first ground together with a mortar and pestle until a homogeneous powder results. The pellet is then pressed in a KBr die at 20,000 psi for 5 min to yield a pellet of 1.00 cm diameter and 0.05 cm thickness. Absorptivity of model compounds Ph_3SiH ($\nu_{\text{Si-H}} = 2118 \text{ cm}^{-1}$ in KBr) and $\text{Ph}_3\text{SiCo}(\text{CO})_4$ ($\nu_{\text{C-O}} = 2092, 2030, 1990 \text{ cm}^{-1}$ in KBr) was determined in KBr and reproducibility was determined to be $\pm 20\%$. Errors for samples including the SiO_2 or Al_2O_3 are even larger. The semi-quantitative infrared measurements show $(\text{S})-\text{SiCo}(\text{CO})_4$ to be air-stable at 25°C for at least several weeks. The relative absorptivities in Table I, relative to $\text{Ph}_3\text{Si-H}$ ($\nu_{\text{Si-H}} = 2118 \text{ cm}^{-1}$) are proportional to concentration and can thus be used to determine concentrations of the $(\text{S})-\text{SiH}$ or $(\text{S})-\text{SiCo}(\text{CO})_4$. The relative absorbance of 1.0 for the 2118 cm^{-1} Si-H stretch in Ph_3SiH corresponds to an absolute absorptivity of 1.0 O.D. units for a 2.54 to 100 weight ratio of Ph_3SiH to KBr in our 1.0 cm diameter, 0.05 cm thick, pellets prepared as described above. Thus, the relative absorbance of 5.5 for $\nu_{\text{C-O}} = 2092 \text{ cm}^{-1}$ of $\text{Ph}_3\text{SiCo}(\text{CO})_4$ means that the absorptivity is 5.5 times that of the 2118 cm^{-1} Si-H stretch of Ph_3SiH for the same number of moles in a given mass of KBr.

To insure that KBr is not reactive when used as a pellet material we have recorded the infrared spectrum of $(S)-SiCo(CO)_4$ and $(S)-SiH_3$ in Nujol mulls. The relative absorptivities are the same as in KBr pellets. Also, the infrared absorbances in KBr are proportional to the signals from Fourier transform infrared photoacoustic spectroscopy of the $(S)-SiCo(CO)_4$ powders.¹³

Results and Discussion

a. Surface Derivatization and Characterization. The synthesis of $(S)-SiCo(CO)_4$ depends on two previous synthetic procedures, equations (1) and (2). The Al_2O_3



and SiO_2 generally have variable amounts of surface $-OH$ depending on prior history of the samples. We have synthesized $(S)-SiCo(CO)_4$ by exploiting the chemistry represented by equations (1) and (2) and have characterized the surfaces by transmission infrared spectroscopy. Representative infrared spectra for a typical $(S)-SiCo(CO)_4$, $(S) = Al_2O_3$, synthesis are shown in Figure 1. The Al_2O_3 is featureless in the $Si-H$ and $C-O$ stretching region. Treatment with $(EtO)_3SiH$ results in a prominent spectral feature at $\sim 2250\text{ cm}^{-1}$. We associate this feature with the $Si-H$ stretch for the surface-confined groups. Reaction of the $(S)-SiH$ powder with $Co_2(CO)_8$ results in a powder that has infrared absorption at ~ 2110 , ~ 2050 , and $\sim 2020\text{ cm}^{-1}$ in accord with a $(S)-SiCo(CO)_4$ system. Note that while we generally find some diminution in the absorption associated with the $Si-H$ stretch, it is not completely absent even after exhaustive reaction with $Co_2(CO)_8$. Table I lists infrared absorptions for $(S)-SiH$; $(S)-SiCo(CO)_4$; and various other systems of relevance to results described below. Included in Table I are data from experiments using Cl_3SiH or Me_2ClSiH , rather than $(EtO)_3SiH$, to introduce $\geq SiH$ functionality on the surface.

Infrared spectroscopy, Table I, reveals the presence, but not the uniformity of coverage, of $\geq SiH$ and $\geq SiCo(CO)_4$ on Al_2O_3 and SiO_2 . The characteristic absorption associated with the $\geq SiH$ is in the range $2134-2257\text{ cm}^{-1}$, depending on the oxide (Al_2O_3 or SiO_2), the starting silane ($(EtO)_3SiH$, Cl_3SiH , or Me_2ClSiH), and the derivatization conditions (H_2O added or not added). A large range of $Si-H$ stretching frequencies is also found for the various silanes measured in alkane solution. Generally, the $Si-H$ stretching frequency would be

expected to be a function of the three remaining groups bonded to the Si atom. The largest difference for surface Si-H stretching frequencies comes from the use of Me_2ClSiH . $\nu_{\text{Si-H}} = 2140 \text{ cm}^{-1}$, compared to using either Cl_3SiH or $(\text{EtO})_3\text{SiH}$. $\nu_{\text{Si-H}} = 2250 \text{ cm}^{-1}$. The 100 cm^{-1} difference is attributable to the presence of the two alkyl groups on the surface Si when using Me_2ClSiH whereas the Cl_3SiH or $(\text{EtO})_3\text{SiH}$ likely result in only oxygen linkages to the surface Si. The value of $\nu_{\text{Si-H}}$ for polymeric material from the reaction of H_2O with $(\text{EtO})_3\text{SiH}$ or Cl_3SiH accords well with the surfaces derivatized with these reagents. Essentially complete hydrolysis of the $(\text{EtO})_3\text{SiH}$ is inferred from the very small signals for C-H stretching absorptions (from EtO- groups) for Al_2O_3 or SiO_2 functionalized with $(\text{EtO})_3\text{SiH}$. For Me_2ClSiH the retention of the methyl groups is directly confirmed by the observation of a C-H stretching absorption at 2985 cm^{-1} for the derivatized surfaces; Me_2ClSiH shows a C-H stretch at 2965 cm^{-1} in CCl_4 solution. The value of $\nu_{\text{Si-H}}$ for Me_2ClSiH , Cl_3SiH , $(\text{EtO})_3\text{SiH}$ and the other Si-H containing materials is consistent with the retention of the two methyl groups when using Me_2ClSiH to functionalize the surface.

Spectral features attributable to the $-\text{Co}(\text{CO})_4$ are also dependent on the nature of the group bonded to the Co. The variation in the Co stretching frequencies for $(\text{EtO})_3\text{SiCo}(\text{CO})_4$, $\text{Et}_3\text{SiCo}(\text{CO})_4$, and $\text{Ph}_3\text{SiCo}(\text{CO})_4$ accord well with the variation for $\text{S}-\text{SiCo}(\text{CO})_4$ depending on whether Me_2ClSiH vs. Cl_3SiH or $(\text{EtO})_3\text{SiH}$ is used as the Si-H source. The two alkyl groups on the Si release electron density (compared to three oxygen groups) such that the $\nu_{\text{C-O}}$ is moved to lower energy presumably reflecting greater π -back bonding to CO from the more electron-rich Co. Thus, for both $\text{S}-\text{SiH}$ and $-\text{Co}(\text{CO})_4$ some molecular level information can be deduced from the infrared spectroscopy. But small differences in band position should not be overinterpreted, since the bands are relatively (compared to solutions) broad. Even for the same sample, some variation ($\pm 3 \text{ cm}^{-1}$) in band maxima can be found from KBr pellet to KBr pellet.

By measuring the absorbance associated with SiH ($\nu_{\text{Si-H}} \approx 2250 \text{ cm}^{-1}$) and SiCo(CO)_4 ($\nu_{\text{CO}} \approx 2025 \text{ cm}^{-1}$) for KBr pellets we have estimated the amount of SiH and SiCo(CO)_4 confined to the oxide surfaces. Results from various preparation procedures using various sources of Al_2O_3 give qualitatively similar results, Table II. Note that SiH persists in every case; some of this functionality may be either structurally or mechanistically inaccessible to the $\text{Co}_2(\text{CO})_8$. The data for the high surface area ($200 \text{ m}^2/\text{g}$) $\gamma\text{-Al}_2\text{O}_3$ pellets, sample #1 in Table II, allow a calculation of average coverage of SiH and SiCo(CO)_4 assuming all of the surface area to be accessible. We calculate an average coverage of $\sim 10^{-12}$ mole of SiCo(CO)_4 and $\sim 3 \times 10^{-11}$ mole of SiH per cm^2 of surface. Similar coverages are found for the high surface area ($400 \text{ m}^2/\text{g}$) SiO_2 , sample #8 of Table II. Taking $\sim 10^{-10} \text{ mol/cm}^2$ to be a monolayer, we find monolayer to sub-monolayer coverage to be a typical result. The coverages from infrared spectroscopy are very approximate, perhaps correct within a factor of three. There are many sources of error including the fact that absorptivities for the Si-H stretch vary considerably, Table I, depending on the environment around the Si and the medium in which the Si-H is dispersed or dissolved. But the qualitative finding of monolayer or sub-monolayer coverage is in accord with determinations of coverage of other functionality, albeit larger groups, using hydrolytically unstable silane reagents.¹⁶ It is noteworthy that -OH absorption in the infrared does not disappear upon functionalization of the oxide powders with either $(\text{EtO})_3\text{SiH}$ or the more reactive Cl_3SiH . Some of the -OH after derivatization could be due to $-\text{Si(H)(OH)}_x$ from the hydrolysis of the $(\text{EtO})_3\text{SiH}$ or Cl_3SiH . Further, it is unlikely that all -OH associated with the hydrated oxides is accessible.

While it may be attractive to conclude that $(\text{EtO})_3\text{SiH}$ or Cl_3SiH functionalize the oxide with a uniform monolayer or less of SiH , such is unlikely. The $(\text{EtO})_3\text{SiH}$ and Cl_3SiH can polymerize and such is known to occur when using $(\text{RO})_3\text{SiR'}$ or $\text{Cl}_3\text{SiR'}$ reagents for modifying chromatographic supports or electrode materials.^{1,2,9} Indeed, unless H_2O can be completely removed the polymerization is probably unavoidable. Removing all of the H_2O would also mean

dehydrating the oxides and coverage of the >SiH on the anhydrous oxides would likely be low. Functionalization of the Al_2O_3 or SiO_2 with Me_2ClSiH provides some indirect information concerning the polymerization, since Me_2ClSiH is not capable of forming the polymers. Surfaces derivatized with Me_2ClSiH have an amount of >SiH , based on infrared absorption, that is not qualitatively different than that from derivatization with Cl_3SiH or $(\text{EtO})_3\text{SiH}$. This likely means polymerization from Cl_3SiH or $(\text{EtO})_3\text{SiH}$ is not extensive. At least, we find that the results are consistent with rather uniform, low coverage of >SiH independent of the source of >SiH . However, as indicated above, the Me_2SiH is electronically different from the >SiH where the three groups bonded to the Si are oxygen.

Another complication in the attachment of $-\text{Co}(\text{CO})_4$ to the oxide supports is that $\text{Co}_2(\text{CO})_8$ reacts rapidly with Lewis bases to give redox products.¹⁷ For example, we find that Al_2O_3 reacts with $\text{Co}_2(\text{CO})_8$ to give a bluish powder. This bluish color also appears when the Al_2O_3 has been first treated with $(\text{EtO})_3\text{SiH}$ to introduce >SiH surface groups prior to reaction with $\text{Co}_2(\text{CO})_8$. We attribute the bluish color to Co^{2+} on the surface; this was confirmed by reacting the $\text{Co}_2(\text{CO})_8$ treated Al_2O_3 with aqueous 1 M HCl. The resulting pink solution showed optical absorption spectral features identical to those for an authentic Co^{2+} sample in aqueous 1 M HCl λ_{max} : 1250, 510, 463 nm.¹⁸ The $\text{Co}_2(\text{CO})_8$ -treated Al_2O_3 shows no C—O infrared stretches attributable to surface confined metal carbonyls. We thus conclude that $\text{Co}_2(\text{CO})_8$ reacts with Al_2O_3 to yield a Co-oxide/hydroxide. Thus, Co-oxide formation appears as a side-reaction accompanying the attachment of $-\text{Co}(\text{CO})_4$ by reaction of $\text{Co}_2(\text{CO})_8$ with the (S)-SiH groups.

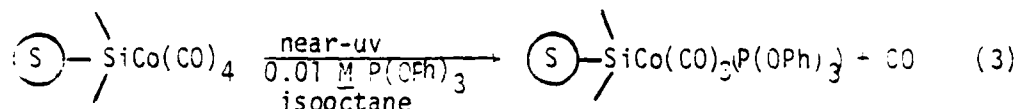
Elemental analyses for some of the Al_2O_3 samples are included in Table II. Non-derivatized samples show little or no detectable Co or Si and samples derivatized with $(\text{EtO})_3\text{SiH}$ but not with $\text{Co}_2(\text{CO})_8$ show the presence of Si but not Co, as expected. The comparison of the elemental analyses with the infrared analyses is revealing. There is apparently far more Si present than can be accounted for by the >SiH and $\text{>SiCo}(\text{CO})_4$. Further, there is far more Co present than can be

accounted for by SiCo(CO)_4 . The infrared determined coverages of SiCo(CO)_4 are consistent ($\pm 20\%$) with the amounts of $\text{Et}_3\text{SiCo(CO)}_4$ that can be detected in solution when SiCo(CO)_4 is irradiated in isooctane as a suspension in the presence of Et_3SiH , vide infra. Thus, the excess Co from the analyses must be due to the Co-oxide/hydroxide formed from the decomposition of $\text{Co}_2(\text{CO})_8$ in the derivatization procedure. Though we do not have a check of SiH as we do for SiCo(CO)_4 , it would seem that the error in % Si from infrared detectable SiH cannot be as large as would be necessary to account for the % Si from elemental analyses. We propose that decomposition of SiH occurs, perhaps by acid-base reactions, to give silicate on the surface. Reaction with $\text{Co}_2(\text{CO})_8$ could lead to decomposition of SiH , but even surfaces that have not been treated with $\text{Co}_2(\text{CO})_8$ give more Si than can be detected as SiH by infrared. A major conclusion from these results is that neither elemental analyses or infrared alone can provide quantitative information concerning the surface functionality present.

From our studies, we conclude that the derivatized oxide particles have a large number of chemical functionalities present. The representation of a derivatized alumina particle in Figure 2 seems justifiable in view of the available infrared data and known reactions. Despite the large number of chemical functionalities, light-activated reactions of the SiCo(CO)_4 can still be studied, owing to the fact that this group can absorb incident light and reactions of this metal carbonyl fragment can be monitored in the C-O stretching region of the infrared without interference from other groups. Photoexcitation of SiCo(CO)_4 , though it is present in dilute

amounts, is analogous to optical excitation of substances in solution at low concentration, exploiting one of the key advantages in optical vs. thermal activation of chemical systems. The absorption onset of $(S)-SiCo(CO)_4$ is expected to occur in the near-uv, based on solution analogues, and consequently, photochemical studies have been carried out using near-uv ($\lambda > 300$ nm) light.

b. Photocchemistry of $(S)-SiCo(CO)_4$ in the Presence of $P(OPh)_3$. Irradiation of deoxygenated 3.0 ml isooctane suspensions of 0.045 g of $(S)-SiCo(CO)_4$, sample #3 in Table II, in the presence of 0.01 M $P(OPh)_3$ yields reactions according to equation (3). Infrared analysis of the supernatant

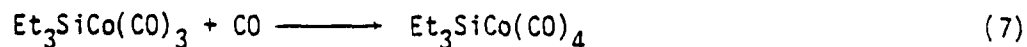
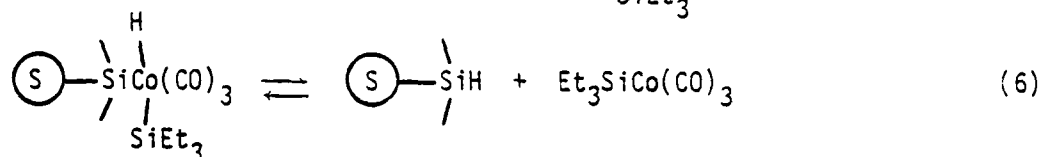
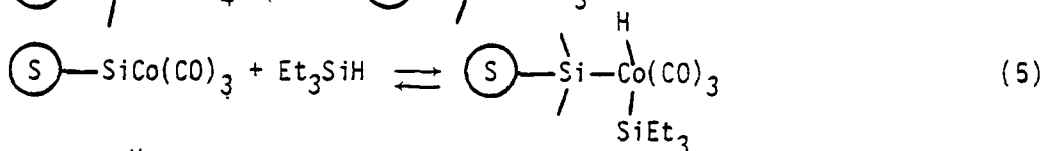
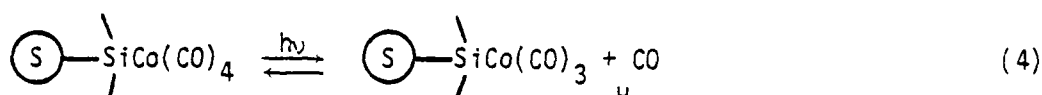


liquid shows no metal carbonyl species. The formation of $Co_2(CO)_6(P(OPh)_3)_2$ would be possible if light-induced cleavage of the Si-Co bond resulted followed by substitution of the released $Co(CO)_4$ radical by $P(OPh)_3$ to yield $Co(CO)_3-(P(OPh)_3)$ radicals that then couple to form $Co_2(CO)_6(P(OPh)_3)_2$.¹⁹ Infrared analysis of the powder after various irradiation times, Figure 3, shows the diminution of absorptions attributable to the $(S)-SiCo(CO)_4$ and the growth of features that are assigned to $(S)-SiCo(CO)_3P(OPh)_3$, Table I. Thus, it appears that CO can be photochemically ejected from $(S)-SiCo(CO)_4$ and Si-Co bond cleavage is apparently unimportant.

Irradiation of $(S)-SiCo(CO)_4$ in isooctane solution containing no deliberately added entering groups results in the diminution of metal carbonyl absorptions in the C-O stretching region. An unidentifiable absorption feature does grow in at 2073 cm^{-1} as a shoulder at intermediate stages of reaction, but the surface would appear to be eventually denuded of metal carbonyls by the near-uv irradiation. The isooctane supernatant exhibits infrared absorptions at positions characteristic of $Co_4(CO)_{12}$, Table I. The yield of this species appears to be ~15%. Both these data and data for

photochemistry in the presence of $P(OPh)_3$ parallel the photochemical data for $R_3SiCo(CO)_4$ in solution.¹²

c. Photochemistry of $(S)-SiCo(CO)_4$ in the Presence of Et_3SiH . Under conditions where CO is photolabilized, irradiation of suspended $(S)-SiCo(CO)_4$ in the presence of Et_3SiH results in the detachment of the $-Co(CO)_4$ from the surface. For example, degassed, 3.0 ml isooctane solutions containing 0.045 g of $(S)-SiCo(CO)_4$, sample #3 of Table II, and 0.5 M Et_3SiH under near-uv irradiation at 25°C yield $Et_3SiCo(CO)_4$ in the supernatant isooctane solution, Figure 4. Analysis of the irradiated powder reveals the diminution of absorptions due to metal carbonyl fragments, Figure 5. The only feature that grows is one at $\sim 2250\text{ cm}^{-1}$ attributable to the regeneration of $(S)-SiH$. Infrared analysis shows that >80% of the surface-confined $-Co(CO)_4$ fragments can be detected as $Et_3SiCo(CO)_4$ in solution. Such data provide confirmation of the coverages of surface-confined $Co(CO)_4$ groups given in Table II. The photochemistry again can be rationalized as resulting from photoinduced loss of CO as the primary photoprocess according to equations (4)-(7), paralleling the solution photo-

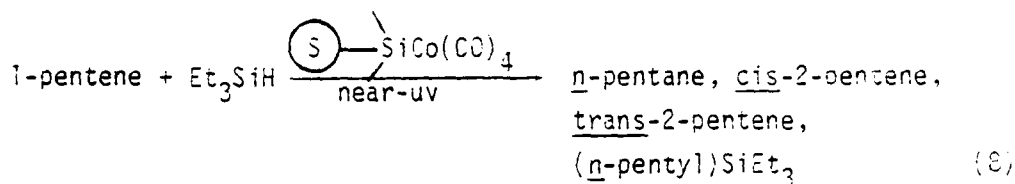


chemical behavior of $R_3SiCo(CO)_4$.¹²

d. Photochemistry of $(S)-SiCo(CO)_4$ Related to Alkene Catalysis. We have previously reported that $R_3SiCo(CO)_4$ is a photochemical precursor to

catalytically active species,¹² despite the fact that Si-Co bond cleavage is not the primary photoprocess. Near-uv irradiation of $(\text{S})-\text{SiCo}(\text{CO})_4$ in isooctane solutions of 1-pentene leads to the generation of $\text{Co}_4(\text{CO})_{12}$ in solution. Infrared analysis of the irradiated powder shows loss of $-\text{Co}(\text{CO})_4$ groups and the growth of weak absorptions in the C-H stretching region that could be due to $(\text{S})-\text{Si}(\text{pentenyl})$. Photolysis of $\text{Et}_3\text{SiCo}(\text{CO})_4$ in the presence of 1-pentene yields $\text{Et}_3\text{Si}(\text{pentenyl})$ as the only Si-containing product.¹² The irradiated powder also shows consumption of $(\text{S})-\text{SiH}$ functionality. Apparently, the Si-H groups not originally reacted with $\text{Co}_2(\text{CO})_8$ can react with photoreleased Co-carbonyl fragments and subsequently with 1-pentene to yield $(\text{S})-\text{Si}(\text{n-pentyl})$; that is, the residual $(\text{S})-\text{SiH}$ reacts with the Co-carbonyl/1-pentene to hydrosilate the 1-pentene. Thus, reaction with alkene and $(\text{S})-\text{SiCo}(\text{CO})_4/(\text{S})-\text{SiH}$ can be induced photochemically. However, there is no accumulation of catalysis products in solution. Even alkene isomerization activity (1-pentene - cis- or trans-2-pentene) is nil.

Irradiation of $(\text{S})-\text{SiCo}(\text{CO})_4$ in the presence of 1/1 mixtures of 1-pentene/ Et_3SiH does result in catalytic chemistry. For example, near-uv irradiation of 0.045 g of $(\text{S})-\text{SiCo}(\text{CO})_4$, sample #3 in Table II, in the presence of 0.39 M $\text{Et}_3\text{SiH}/0.39$ M 1-pentene in isooctane rapidly yields infrared detectable metal carbonyls in the supernatant solution. Initially, $\text{Et}_3\text{SiCo}(\text{CO})_4$ is formed, and irradiation also yields infrared absorptions in the supernatant at 1960 cm^{-1} and 1966 cm^{-1} (sh) that have been previously observed, but not unambiguously assigned,^{12,15} in solutions initially containing $\text{Co}_2(\text{CO})_8/1\text{-pentene}/\text{Et}_3\text{SiH}$. Gas chromatographic analysis of the solution after 48 min of irradiation shows the following composition (% based on initial 1-pentene concentration): n-pentane (4.2); 1-pentene (1.3); trans-2-pentene (46.3); cis-2-pentene (15.5); (n-pentyl) SiEt_3 (32.7). Thus, photocatalysis is effected, equation (8). On the timescale of this experiment



there is no thermal catalysis. Further, Al_2O_3 , Al_2O_3 treated only with $\text{Co}_2(\text{CO})_8$, or Al_2O_3 treated only with $(\text{EtO})_3\text{SiH}$ gives neither thermal or photoinduced catalysis under the same conditions. Thus, the $(\text{S})-\text{SiCo(CO)}_4$ would appear to be a photochemical precursor to catalysis. In view of the photogeneration of $\text{Et}_3\text{SiCo(CO)}_4$ from $(\text{S})-\text{SiCo(CO)}_4$, equations (4)-(7), in the presence of Et_3SiH or in the presence of Et_3SiH /1-pentene, catalysis should result if for no other reason than $\text{Et}_3\text{SiCo(CO)}_4$ yields catalysis when irradiated in the Et_3SiH /1-pentene mixture.¹²

Irradiation of $(\text{S})-\text{SiCo(CO)}_4$ in the presence of neat 1/1 Et_3SiH /1-pentene results in catalytic chemistry. Data for a typical photocatalysis run are included in Table III. No dark reaction occurs on the timescale of this experiment. Infrared analysis of the $(\text{S})-\text{SiCo(CO)}_4$ shows >95% loss of $-\text{Co(CO)}_4$ from the Al_2O_3 surface at ~30 min irradiation time. Analysis of the solution shows the growth of the absorptions at $\sim 1960 \text{ cm}^{-1}$ found in thermal reactions of $\text{Co}_2(\text{CO})_8$ with Et_3SiH /1-pentene¹⁵ and photoreactions of $\text{Et}_3\text{SiCo(CO)}_4$ with Et_3SiH /1-pentene.¹² At longer irradiation times infrared bands for $\text{Et}_3\text{SiCo(CO)}_4$ become apparent and the 1960 cm^{-1} feature intensifies somewhat. After 375 min, there are no detectable Co-carbonyl fragments on the surface of the Al_2O_3 . The mol % of Si-H in the Al_2O_3 decreases during the irradiation, likely reflecting the generation of $(\text{S})-\text{Si(n-pentyl)}$.

The main conclusion regarding catalysis from the irradiations of $(\text{S})-\text{SiCo(CO)}_4$ in the presence of Et_3SiH /1-pentene is that the bulk of the catalysis occurs from the photoreleased Co-carbonyl fragments. For example, in the particular run detailed in Table III, most (>95%) of the Co-carbonyl is in homogeneous solution after the ~30 min irradiation time. To provide

additional confirmation of this conclusion, 0.0759 g of $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ sample #3 in Table II, was irradiated in 1 ml of neat Et_3SiH until -30° (~ 80 min irradiation) of the $-\text{Co}(\text{CO})_4$ was present in solution as $\text{Et}_3\text{SiCo}(\text{CO})_4$. The supernatant was diluted with 1-pentene to bring the $\text{Et}_3\text{SiH}/1\text{-pentene}$ to a 1/1 mole ratio. Irradiation of the $\text{Et}_3\text{SiCo}(\text{CO})_4/\text{Et}_3\text{SiH}/1\text{-pentene}$ gave photocatalytic action with a rate and product distribution very similar to that when the $\text{Si}(\text{C}_6\text{H}_5)_3\text{H}/\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ phase was not removed. The catalytic products and their initial ratios accord well with previous findings in this laboratory from thermal catalysis using $\text{Co}_2(\text{CO})_8$ or photocatalysis using $\text{Et}_3\text{SiCo}(\text{CO})_4$.¹² Thus, we firmly conclude that photocatalytic action from $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ results from reactive Co-carbonyl fragments released into homogeneous solution. The active species appears to be the same as that involved in $\text{Co}_2(\text{CO})_8$ or $\text{Et}_3\text{SiCo}(\text{CO})_4$ catalysis.

e. Photocatalysis Results Under Variable Conditions. Photocatalysis of $\text{Et}_3\text{SiH}/1\text{-pentene}$ mixtures has been carried out using various preparations of $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ and under variable conditions. Table IV details results for various preparations of $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ where the major variable would appear to be the amount of $-\text{Co}(\text{CO})_4$ actually added when 0.045 g/ml of $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ is added to the mixture. Note that the irradiation source (355 ± 20 nm, 2×10^{-6} ein/min) for the experiments summarized in Table IV has lower intensity than for the Pyrex filtered 450 W Hg-arc used for the experiments summarized in Table III. Accordingly, the reaction times are longer. Variations in the activity of the $\text{Si}(\text{C}_6\text{H}_5)_3\text{Co}(\text{CO})_4$ system crudely parallel the expectations for rate of release of $-\text{Co}(\text{CO})_4$. Higher coverages and large surface areas provide for a higher rate of appearance of active material in solution. All of the catalyst precursors yield the same Si-containing product, namely $\text{Et}_3\text{Si}(\text{n-pentyl})$ and rather small amounts of n-pentane. In cases where there is significant dark reaction at 25°C on the 69 h timescale we also find very rapid photocatalytic action. The thermal activity in the dark is attributable to a slow thermal process again involving

loss of CO as the rate limiting step. However, under all conditions the light-activated catalysis proceeds more rapidly even at the low light intensity. For the data given in Table III, where the 450 W Hg-arc source was used, the dark thermal controls show little or no reaction on the timescale of the experiments summarized.

Table III includes data for reactions carried out in neat 1/1 Et₃SiH/1-pentene mixtures exposed to H₂ or H₂/CO mixtures. The data show that the product distribution under 4 psig H₂ shifts markedly to higher yields of n-pentane. However, irradiation of $\text{S} \rightarrow \text{SiCo(CO)}_4$ in the presence of neat 1-pentane and 4 psig H₂ yields little isomerization or hydrogenation. These results are consistent with our previous findings for photoactivation of alkene catalysis using Co-carbonyl species: H₂ as an oxidative addition substrate to create hydrides for isomerization or reduction does not seem to be effective.²⁰ The H₂/CO atmosphere suppresses the rate of catalysis even at the 4 psig CO pressure used. The resulting product mixture contains no detectable hydroformylation products. The suppression of catalysis is associated with the capture of coordinatively unsaturated sites by the CO. The effects of H₂ and H₂/CO parallel those found earlier for photocatalysis of alkene reactions using Co-carbonyl species.^{12,20}

The ability to functionalize $\text{S} \rightarrow \text{SiCo(CO)}_4$ by photosubstitution affords an opportunity to examine the photocatalytic activity of $\text{S} \rightarrow \text{SiCo(CO)}_3\text{P(OPh)}_3$. Irradiation of $\text{S} \rightarrow \text{SiCo(CO)}_4$ in the presence of P(OPh)₃ followed by decanting and washing yields a mixture of $\text{S} \rightarrow \text{SiCo(CO)}_3\text{P(OPh)}_3$ and $\text{S} \rightarrow \text{SiCo(CO)}_4$. Use of this mixture as a catalyst precursor compared to pure $\text{S} \rightarrow \text{SiCo(CO)}_4$ under the same conditions yields an important difference in the catalytic products, Table V. The formation of at least two isomers of Et₃Si(pentenyl) accompanies the usual distribution of products. Such products have previously been found from the thermal and photocatalyzed reaction of Et₃SiH/1-pentene mixtures using Fe(CO)₅^{21,22}

and $M_3(CO)_4$ ($M = Fe, Ru, Os$).²³ Another difference in the product distribution is the lower initial trans/cis ratio of the 2-pentene isomers compared to the catalyst having no $P(OPh)_3$ present. Analysis of the $(S)-SiCo(CO)_4/(S)-SiCo(CO)_3(P(OPh)_3)$ powder shows loss of Co-carbonyl species, again indicating that the catalysis occurs via photo-released Co-carbonyl fragments. The very different product ratio with the $P(OPh)_3$ complex indicates that the actual catalyst is different than that for $(S)-SiCo(CO)_4$. It is attractive to conclude that CO loss is again the primary photoreaction leaving $P(OPh)_3$ in the coordination sphere to influence product ratios by steric and electronic effects. The catalytic activity appears to be somewhat lower than for the unsubstituted $(S)-SiCo(CO)_4$. This is very likely due to lower quantum yields for the primary process of CO loss from the $P(OPh)_3$ complex.

f. Comparison of Catalytic Activity of $(S)-SiCo(CO)_3$ with $Co_2(CO)_8$.

Photoexcitation of $(S)-SiCo(CO)_4$ in the presence of 1-pentene/ $HSiEt_3$ mixtures apparently yields the same catalyst species that results from the irradiation of $Et_3SiCo(CO)_4$.¹² Further, we have previously concluded that the irradiation of $Et_3SiCo(CO)_4$ leads to the active species formed thermally from $Co_2(CO)_8$.^{12,15} Thus, comparison of the catalytic activity of $Co_2(CO)_8$ and $Et_3SiCo(CO)_4$ is appropriate. We have examined the initial thermal activity of $Co_2(CO)_8$ at 20°C for isomerization and hydrosilation of 1-pentene under the same conditions where we can photoactivate the $(S)-SiCo(CO)_4$ system. Data in Table VI are representative of the activity of the two different precursor systems. In both systems the isomerization products are formed at a faster rate than the hydrosilation products and it would appear that the rate of formation of hydrosilation products declines as the 1-pentene is converted to the 2-pentenenes. This is reasonable, since it is likely that the hydrosilation of 1-pentene is more rapid than the same

reaction of the internal isomers. The interesting finding is that the photoactivated system is in fact quite similar in turnover rate to the $\text{Co}_2(\text{CO})_8$ thermal system. Further, since the observed rate of product formation depends on excitation rate (light intensity) the turnover rate for the photoactivated system could be even higher at higher light intensity. In both systems it would appear that the isomerization turnover number is similar; we find that the number of product molecules formed is generally limited by substrate concentration not catalyst lifetime. For hydrosilation, we have already demonstrated that illumination of $\text{Et}_3\text{SiCo}(\text{CO})_4$ allows more turnovers for (n-pentyl) SiEt_3 formation, since the $\text{Co}_2(\text{CO})_8$ thermal system ultimately ceases activity due to formation of $\text{Et}_3\text{SiCo}(\text{CO})_4$ that is not thermally active.

Irradiation of species such as $\text{R}_3\text{SiCo}(\text{CO})_4$ does result in persistent thermal activity in the dark at 20°C . However, the activity is relatively low and short-lived. For example, a flash excitation of $\text{Ph}_3\text{SiCo}(\text{CO})_4$ leads to ~50% dark isomerization of 1 M 1-pentene in the presence of 1 M HSiEt_3 during a 4 h period. Continuous irradiation leads to nearly complete equilibration of the linear pentenes under the same conditions in <4 h. Thus, considerable activity can persist in the dark, but irradiation accelerates the catalytic rate even further.

Summary

The data adequately demonstrate that $-\text{Co}(\text{CO})_3$ anchored to oxide surfaces via reaction of $\text{Co}_2(\text{CO})_8$ with $\text{S}-\text{SiH}_3$ exhibits photochemistry that parallels that for solution $\text{R}_3\text{SiCo}(\text{CO})_4$ analogues. The photoinduced loss of CO is the principal result of photoexcitation of either $\text{R}_3\text{SiCo}(\text{CO})_4$ in solution¹² or $\text{S}-\text{SiCo}(\text{CO})_4$ suspended in solutions. In neither case do we find evidence for prompt scission of the Co-Si bond, but in each case reaction with R_3SiH or alkenes leads to chemically efficient loss of the original Co-Si bond. For $\text{S}-\text{SiCo}(\text{CO})_4$ this means that the Co-carbonyl species does not remain anchored to the surface. Thus, with this system we have not achieved the capability of "matrix isolating" photogenerated, coordinatively unsaturated intermediates. However, the $\text{S}-\text{SiCo}(\text{CO})_4$ system as a catalyst precursor is easily handled and is less sensitive to O_2 than is the solution species $\text{Et}_3\text{SiCo}(\text{CO})_4$. The concept of releasing a catalyst photochemically at a rate controlled by light intensity is one that could be exploited, in principle, in catalytic reactions.

Acknowledgements. We thank the Office of Naval Research for partial support of this research. Support from the Dow Chemical Company is also gratefully acknowledged. Support for the Fourier transform infrared spectrometer was supplied by the National Institutes of Health, grant number GM 27551.

References

1. Murray, R. W. Accs. Chem. Res., 1980, 13, 135.
2. Karger, B.L.; Giese, R.W. Anal. Chem., 1978, 50, 1040A.
3. (a) Arkles, B., Chem. Tech., 1977, 7, 766; (b) Whittenurst, D.C. Chemtech, 1980, 10, 44.
4. Bailey, D.C.; Langer, S.H. Chem. Rev., 1981, 81, 109.
5. Hartley, F.R.; Vezey, P.N. Adv. Organomet. Chem., 1977, 17, 189.
6. Grushka, E.; Kikta, E.J. Anal. Chem., 1977, 49, 1004A.
7. Collman, J.P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F.C. J. Am. Chem. Soc., 1980, 102, 6027.
8. Degrand, C.; Miller, L.L. J. Am. Chem. Soc., 1980, 102, 5728.
9. Bolts, J.M.; Bocarsly, A.B.; Palazzotto, M.C.; Walton, E.G.; Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 1378.
10. Bookbinder, D.C.; Bruce, J.A.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. Proc. Natl. Acad. Sci., U.S.A., 1980, 77, 6280.
11. Sanner, R.D.; Austin, R.G.; Wrighton, M.S.; Honnick, W.D.; Pittman, C.U., Jr. Inorg. Chem., 1979, 18, 928.
12. Reichel, C.L.; Wrighton, M.S. Inorg. Chem., 1980, 19, 3858.
13. Kinney, J.B.; Staley, R.H.; Reichel, C.L.; Wrighton, M.S. J. Am. Chem. Soc., 1981, 103, 0000.
14. Hatchard, C.G.; Parker, C.A. Proc. Roy. Soc. A, 1956, 235, 518.
15. Chalk, A.J.; Harrod, J.F. J. Am. Chem. Soc., 1967, 89, 1640.
16. Fischer, A.B.; Kinney, J.B.; Staley, R.H.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 6501.
17. Wender, I.; Sternberg, H.W.; Orchin, M. J. Am. Chem. Soc., 1952, 74, 1216.
18. Figgis, B.N. "Introduction to Ligand Fields", Wiley: New York, 1966, p. 223.
19. Brown, T.L.; Absi-Halabi, M. J. Am. Chem. Soc., 1977, 99, 2982.
20. Reichel, C.L.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 6769.
21. Nesmeyanov, A.N.; Friedlina, R.K.; Chukovskaya, E.C.; Petrova, R.G.; Belyavsky, A.B. Tetrahedron, 1961, 17, 61.
22. Schroeder, M.A.; Wrighton, M.S. J. Organometal. Chem., 1977, 128, 345.
23. Austin, R.G.; Paonessa, R.S.; Giordano, P.J.; Wrighton, M.S. Adv. Chem. Ser., 1978, 168, 189.

Table I. Infrared Spectra of Surface-Confined Species and Relevant Species for Comparison.

Species	Medium	Key IR Band(s), cm^{-1} (s or rel. abs.) ^c
$(\text{EtO})_3\text{SiCo}(\text{CO})_4$ ^a	heptane	2105(0.29), 2040(0.81), 2025(0.26), 2010(1.00)
$\text{Et}_3\text{SiCo}(\text{CO})_4$	cyclohexane	2089(2740), 2026(4390), 1995(3580), 1992sh (3000)
$\text{Ph}_3\text{SiCo}(\text{CO})_4$	cyclohexane	2093(3250), 2032(3720), 2003(7000)
	KBr ^b	2092(5.5) ^b , 2030(5.5) ^b , 1990(7.4, 7.7) ^b
$\text{Ph}_3\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ ^c	cyclohexane	2049(0.11), 1980(0.32), 1973(1.00)
$\text{Et}_3\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ ^c	hexane	2035(0.35), 1968(0.98), 1963(1.00)
$(\text{EtO})_3\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ ^c	isooctane	1987(1.00), 1974(0.78)
$\text{Co}_4(\text{CO})_{12}$	cyclohexane	2062(12550), 2053(14,000), 2037(930), 2025(1590), 2020sh(930), 1864(4890)
$\text{Ph}_3\text{Si-H}$	cyclohexane	2129(204)
	isooctane	2126(214)
	KBr ^b	2118(1.0) ^b
$(\text{EtO})_3\text{Si-H}$	isooctane	2196(135)
	neat	2195(--)
$\text{Et}_3\text{Si-H}$	isooctane	2100(149)
$\text{Cl}_3\text{Si-H}$	heptane	2250(--)
$\text{Me}_2\text{ClSi-H}$	isooctane	2165(223)
$[\text{O}_3\text{Si-H}]_n$	neat	2246
(from $(\text{EtO})_3\text{SiH} + \text{H}_2\text{O}$)	Nujol mull	2253
	KBr	2256
$[\text{O}_3\text{Si-H}]_n$		
(from $\text{Cl}_3\text{SiH} + \text{H}_2\text{O}$)	Nujol mull	2252
$\textcircled{\text{S}}-\text{Si-H}$ (from $(\text{EtO})_3\text{SiH}$)	KBr	
$\textcircled{\text{S}} = \text{Al}_2\text{O}_3$		2257 (H_2O added); 2239(dry)
$\textcircled{\text{S}} = \text{SiO}_2$		2248 (dry)
$\textcircled{\text{S}}-\text{SiCo}(\text{CO})_4$ (from $(\text{EtO})_3\text{SiH}$)	KBr	
$\textcircled{\text{S}} = \text{Al}_2\text{O}_3$ (dry)		2109(0.27), 2051(0.58), 2023(1.00)
$\textcircled{\text{S}} = \text{Al}_2\text{O}_3(\text{H}_2\text{O added})$		2111(0.40), 2054(0.66), 2024(1.00)
$\textcircled{\text{S}} = \text{SiO}_2$		2108(0.29), 2048(0.51), 2020(1.00)

Table I. (continued)

Species	Medium	Key IR Band(s), cm^{-1} , or rel. abs. ^a
$\text{S} \begin{array}{c} \diagup \\ \text{SiCo(CO)}_3\text{P(OPh)}_3 \end{array}$ $\text{S} = \text{Al}_2\text{O}_3$ $\text{S} = \text{SiO}_2$	KBr	2060(0.21), 1995(1.00), 1985(0.91)
$\text{S} \begin{array}{c} \diagup \\ \text{Si-H (from HSiCl}_3\text{)} \end{array}$ $\text{S} = \text{Al}_2\text{O}_3$	KBr	2059(0.10), 1991(1.00), 1923(0.39)
$\text{S} \begin{array}{c} \diagup \\ \text{SiCo(CO)}_4 \text{ (from HSiCl}_3\text{)} \end{array}$ $\text{S} = \text{Al}_2\text{O}_3$	KBr	2263(H_2O added); 2257(dry)
$\text{S} \begin{array}{c} \diagup \\ \text{SiMe}_2\text{-H (from Me}_2\text{ClSiH)} \end{array}$ $\text{S} = \text{Al}_2\text{O}_3$ $\text{S} = \text{SiO}_2$	KBr	2114(0.30), 2054(0.49), 2025(1.00)
$\text{S} \begin{array}{c} \diagup \\ \text{SiMe}_2\text{Co(CO)}_4 \end{array}$ $\text{(from Me}_2\text{ClSiH)}$ $\text{S} = \text{SiO}_2$	KBr	2134 2148 2100(0.25), 2039(0.48), 2009(1.00)

^aGenerated in situ by reaction of $\text{Co}_2(\text{CO})_8$ with $(\text{EtO})_3\text{SiH}$ in heptane.

^bUnderlined values in parentheses are for "model" complexes in KBr relative to the 2118 cm^{-1} Si-H stretch in Ph_3SiH . O.D. was determined to be proportional to concentration in KBr; cf. Experimental. These absorptivities are absolute and allow the coverage calculations for SiCo(CO)_4 and SiH assuming similar absorptivities for the various bands, Table II.

^cGenerated in situ by 355 nm irradiation of appropriate $\text{R}_3\text{SiCo(CO)}_4$ in the presence of 0.01 M P(OPh)_3 ; cf. ref. 12.

^dValues in parentheses are relative absorbance (relative to most intense band for the substance = 1.00), extinction coefficient in solutions, or quantitative absorbance relative to Ph_3SiH , cf. Experimental and note b above.

Table II. Typical Coverages of γ -SiI and γ -SiCo(CO)₄ Synthesized by Various Procedures.^a

Oxide	Sample #	Procedure ^b	Analysis from Infrared ^c		Elemental Analyses ^d	
			Mol % SiI	Mol % SiCo(CO) ₄	% Si (calcd)	% Co (calcd)
γ -Al ₂ O ₃ (powdered) ^e	0	Not Derivatized	0	0	0.09(0)	0.009(0)
	0"	III, but no Co ₂ (CO) ₈	4.00	0	3.03(1.15)	0(0)
	0'''	III, but no Co ₂ (CO) ₈	2.86	0	3.43(0.81)	0(0)
γ -Al ₂ O ₃ (pellets)	1	I	1.3	0.05	2.16(0.36)	0.84(0.03)
	1'	I, but no Co ₂ (CO) ₈	1.99	0	2.62(0.56)	0(0)
	1''	I	1.6	0.14	2.53(0.49)	0.47(0.08)
γ -Al ₂ O ₃ (powdered) ^e	2	II	2.7	0.4	2.51(0.90)	0.72(0.25)
	3	III	2.7	0.9		
	4	IV	1.1	0.2		
	5	V	1.3	0.4		
	6	VI	2.4	0.5	3.66(0.50)	1.03(0.25)
	7	Not Derivatized	0	0	0.05(0)	0.009(0)
Woelm Al ₂ O ₃	7'	III	0.5	0.03	2.06(0.15)	0.55(0.02)
SiO ₂ (400 m ² /g)	8	VII	2.92(Prior to Co ₂ (CO) ₈)	----		
			2.88(After Co ₂ (CO) ₈)	0.25		
	8'	IV	6.1 (Prior to Co ₂ (CO) ₈)	----		
			3.4 (After Co ₂ (CO) ₈)	1.9		
Al ₂ O ₃ (powdered) ^e	9	VII	0.15 (Prior to Co ₂ (CO) ₈)	----		
			0.15 (After Co ₂ (CO) ₈)	Detectable		

Table II. (continued)

Derivatization procedure is generally	Al_2O_3	$(\text{EtO})_3\text{SiH}$ 25°C	$\text{Co}_2(\text{CO})_8$ 25°C
<p>^a Derivatization procedure is generally Al_2O_3 25°C $(\text{EtO})_3\text{SiH}$ 25°C $\text{Co}_2(\text{CO})_8$ 25°C.</p> <p>^b I, derivatized under anhydrous conditions; the $(\text{S})-\text{SiH}$ intermediate was not isolated prior to $\text{Co}_2(\text{CO})_8$ reaction. II, same as I but a very large excess (25X vs. usual 5X) of $(\text{EtO})_3\text{SiH}$ was used. III, same as II but H_2O (0.12 ml) added during reaction with $(\text{EtO})_3\text{SiH}$. IV, same as I but $(\text{S})-\text{SiH}$ was isolated prior to reaction. V, same as IV but H_2O (0.12 ml) added during reaction with $(\text{EtO})_3\text{SiH}$. VI, same as V but very large excess of $(\text{EtO})_3\text{SiH}$ was used. VII, functionalized with Me_2ClSiH as in <u>Experimental</u>.</p>			

^c Coverages are approximated by infrared spectroscopy, 2250 cm^{-1} for $-\text{Si}-\text{H}$ and 2020 cm^{-1} for $-\text{SiCo}(\text{CO})_4$, see Table I and Experimental. The mol % refers to the ratios of SiH or $\text{SiCo}(\text{CO})_4$ to moles of SiO_2 or Al_2O_3 times 100%.

^d Elemental analyses (Galbraith) for Si and Co (% by weight) were performed for some of the samples. The % by weight of Si and Co from the infrared data are given in parentheses. These calculated values would be for Co as $-\text{SiCo}(\text{CO})_4$ and Si as $-\text{SiH}$ plus $-\text{SiCo}(\text{CO})_4$. The Co and Si present as oxide from decomposition is thus significant, see text.

^e Powdered $\gamma\text{-Al}_2\text{O}_3$ is from pulverized $\gamma\text{-Al}_2\text{O}_3$ pellets of 200 m^2/g surface area.

Table III. Photocatalyzed Reactions of 1-Pentene.^a

hν, min	INITIAL CONDITIONS				PRODUCT DISTRIBUTION (% OF TOTAL)				
	1-penteneM	HSiEt ₃ M	H ₂ ,psig	CO,psig	n-pentane	1-pentene	trans-2-pentene	cis-2-pentene	1,3-(n-pentyl)
120	3.26	3.26	4	0	10.2	2.4	60.7	17.1	9.7
120	3.26	3.26	0	0	1.0	2.5	71.6	16.1	8.7
135	9.14(neat)	0	4	0	0.22	95.5	3.2	1.1	---
165	9.14(neat)	0	4	4	0.19	97.8	1.6	0.33	---
165	3.26	3.26	4	4	1.5	76.1	15.5	3.9	3.0
0	3.26	3.26	0	0	0	99.1	0.71	0.22	0
28					0	94.5	3.5	1.3	0.68
56					0.34	74.1	17.2	3.8	4.3
91					0.75	29.7	42.9	4.4	22.2
124					1.6	3.3	58.7	12.6	23.9
148					1.5	4.7	55.7	12.0	26.1

^aPhotocatalyst is $\text{S} \begin{array}{c} \diagup \\ \text{---} \text{SiCo(CO)}_4 \end{array}$ (sample #3 of Table II); 0.045g of this powder was suspended in 1.0 ml of the indicated solution and deoxygenated. Irradiation was at 25°C using a Pyrex filtered 450 W Hg-arc lamp under the same conditions for each sample. Analyses were by gas chromatography. All samples were stirred during the irradiation. On the timescale of these experiments no thermal reaction is detectable in the dark.

Table IV. Photocatalysis of Neat 1:1 1-Pentene/H₂SiEt₃ Solutions by Various Preparations of $\text{Si}(\text{CO})_4$ ^a

Support	Irrdn Time, h	PRODUCT DISTRIBUTION, %				
		n-pentane	1-pentene	trans-2-pentene	cis-2-pentene	Et ₃ Si(n-pentyl)
SiO ₂ powder (low sur- face area; low coverage of -Co(CO) ₄)	0	0.032	99.7	0	0.19	0
	4.25	0.96	28.9	60.8	5.4	4.0
	12	1.3	1.6	75.4	14.6	7.2
	69	1.9	0.94	48.0	1.5	45.7
	69 (dark) ^b	0.084	96.8	2.9	0.17	0.25
Gamma- Al ₂ O ₃ pellets (sample #1 of Table II)	0	0.032	99.7	0	0.20	0
	4.25	0.030	99.8	0	0.12	0.061
	12	0.14	92.1	7.1	0.26	0.47
	24	2.6	4.4	77.6	10.6	4.8
	69	1.7	2.3	80.6	10.2	5.3
	69 (dark) ^b	0.11	99.1	0.78	0.034	0.067
Woelm Al ₂ O ₃ (Sample #7 ^a of Table II)	0	0.029	99.8	0	0.12	0
	4.25	0.94	86.3	11.5	0.62	0.53
	24	2.6	16.5	69.1	8.7	3.0
	69	3.9	2.0	87.4	2.3	4.3
	69 (dark) ^b	0	99.9	0	0.14	0
γ-Al ₂ O ₃ Powder (Sample #2 of Table II)	0	0.032	99.8	0	0.19	0
	4.25	0.63	80.9	16.6	0.83	1.1
	12	1.7	24.1	67.6	2.5	4.1
	69	2.4	1.6	86.0	1.0	9.0
	69 (dark) ^b	1.2	12.5	73.6	8.0	4.6
γ-Al ₂ O ₃ Powder (Sample #3 of Table II)	0	0.031	99.7	0	0.19	0
	0.5	0.22	93.5	5.0	0.94	0.40
	1.0	0.64	64.0	29.2	3.4	2.8
	4.25	3.1	1.6	86.2	1.3	8.0
	64	13.0	0.14	9.6	1.9	74.5
	64 (dark) ^b	2.6	16.0	76.3	0.36	4.9

^a 0.045 g of $\text{Si}(\text{CO})_4$ in 1 ml of degassed H₂SiEt₃/1-pentene irradiated at 355 nm at 2×10^{-6} ein/min at 25°C. All solutions were stirred.

Table IV. (continued)

b₁(dark) denotes samples that were treated in parallel with other samples for the indicated time but were not exposed to light.

Table V. Comparison of Catalytic Properties of SiCo(CO)_4 and SiCo(CO)_4 and $\text{SiCo(CO)}_3(\text{P(olPh)}_3)$.^a

Attached Catalyst	hν(min)	n-pentane	l-pentene	PRODUCT DISTRIBUTION (%)			Isomers of $\text{Et}_3\text{Si(penteny)}_2$
				trans-2-pentene	cis-2-pentene	$\text{Et}_3\text{Si(n-pentyl)}$	
SiCo(CO)_4 (sample #2 of Table II)	0	0	100	0	0	0	0
	45	0.46	57.8	36.5	3.2	2.0	0
	60	0.68	25.9	63.7	7.9	1.8	0
	75	0.99	21.5	66.6	7.7	3.2	0
	250	1.6	3.4	77.6	12.3	5.1	0
	250(dark) ^b	0	100	0	0	0	0
SiCo(CO)_{n-4-n} $n = 4, 25.6\%$ $n = 3, 74.4\%$ $L = \text{P(OPh)}_3$ (From sample #2 of Table II by photosubstitution)	0	0	100	0	0	0	0
	30	0	98.9	0.40	0.19	0.28	0.028
	45	0.18	95.7	2.7	0.15	0.93	0.085
	75	0.42	83.1	10.1	0.92	4.3	0.39
	278	2.3	1.9	63.1	19.9	9.5	1.3
	278(dark) ^b	0	100	0	0	0	0

^a 0.045 g of SiCo(CO)_{n-4-n} in degassed 1.0 ml 1/1 $\text{Et}_3\text{SiH}/1$ -pentene solution irradiated at 25°C through Pyrex using a 450 W Hg-arc lamp. Solutions were analyzed by gas chromatography to determine composition. All samples were stirred during irradiation.

^b (dark) denotes samples that were treated in parallel with other samples for the indicated time but were not exposed to light.

Table VI. Comparison of Catalytic Activity of $(\text{S})-\text{SiCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$.^a

Catalyst Precursor	Substrates	Time, min (Δ or $h\nu$)	% Conversion ^b	Product ^c	Turnover Rate, h^{-1} ^d
$\text{Co}_2(\text{CO})_8$ (0.002 M)	1-pentene/ HSiEt_3 (3.26 M/3.26 M)	14 (Δ)	28.4	2-pentenes	1000
		24 (Δ)	54.4	2-pentenes	1100
		54 (Δ)	82.0	2-pentenes	750
		179 (Δ)	>85	2-pentenes	Equilibrium Attained ^e
$\text{Co}_2(\text{CO})_8$ (0.002 M)	1-pentene/ HSiEt_3 (3.26 M/3.26 M)	96 (Δ)	12.3	(\underline{n} -pentyl) SiEt_3	125
		237 (Δ)	15.5	(\underline{n} -pentyl) SiEt_3	60
		495 (Δ)	16.0	(\underline{n} -pentyl) SiEt_3	32
$(\text{S})-\text{SiCo}(\text{CO})_4$ (0.004M) ^f	1-pentene/ HSiEt_3 (3.26 M/3.26 M)	56 ($h\nu$)	21.0	2-pentenes	180
			4.0	(\underline{n} -pentyl) SiEt_3	35
		91 ($h\nu$)	47.3	2-pentenes	250
			22.2	(\underline{n} -pentyl) SiEt_3	120
		124 ($h\nu$)	71.3	2-pentenes	Equilibrium Attained ^e
			23.9	(\underline{n} -pentyl) SiEt_3	90

^a Samples of $(\text{S})-\text{SiCo}(\text{CO})_4$ or $\text{Co}_2(\text{CO})_8$ in deoxygenated 3.26 M/3.26 M 1-pentene/ HSiEt_3 were reacted at 20°C in the dark ($\text{Co}_2(\text{CO})_8$) or under illumination from a 450 W Hanovia Hg-arc ($(\text{S})-\text{SiCo}(\text{CO})_4$).

^b % Conversion to indicated products based on 1-pentene.

^c The products from catalysts are the 2-pentenes and (\underline{n} -pentyl) SiEt_3 ; cf. Tables III-V.

^d Turnover rate is the number of product molecules formed per hour per Co atom initially added as either $\text{Co}_2(\text{CO})_8$ or $(\text{S})-\text{SiCo}(\text{CO})_4$.

^e At this point the linear pentenes are close to the thermodynamic ratio.

^f This concentration is the total effective $-\text{Co}(\text{CO})_4$ concentration assuming the $-\text{Co}(\text{CO})_4$ to be completely efficiently released. The sample used is #3 of Table II and data are from Table III.

Figure Captions

Figure 1. Infrared spectral changes accompanying the progressive derivatization of a naked alumina surface. Curve A refers to the surface before reaction; curve B after reaction with $\text{HSi}(\text{OEt})_3$; curve C after reaction with $\text{HSi}(\text{OEt})_3$ and subsequently $\text{Co}_2(\text{CO})_8$. Note that left scale is for A and B and right scale is for C.

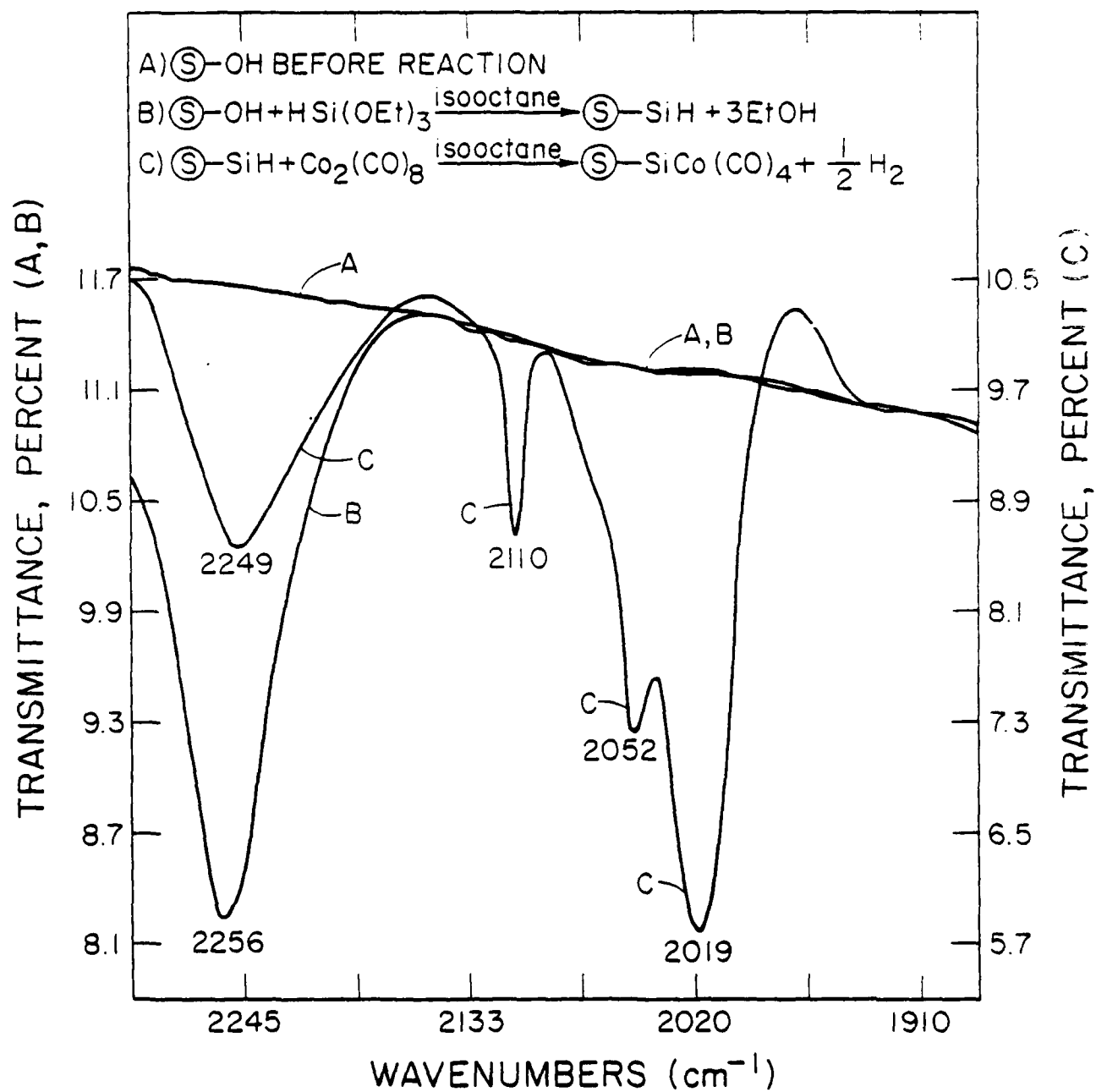
Figure 2. Representation of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ at various stages in the derivatization to confine $\text{Co}(\text{CO})_4$ to the surface.

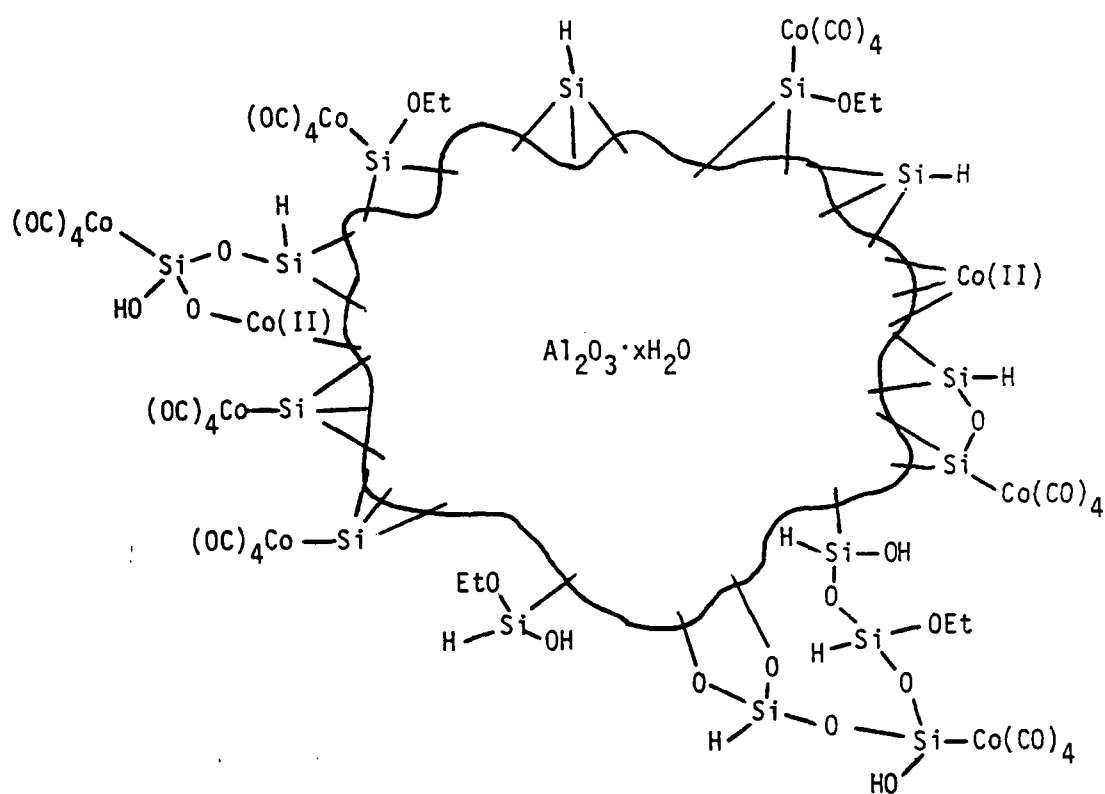
Figure 3. Infrared spectral changes during the irradiation of a derivatized alumina surface in the presence of $\text{P}(\text{OPh})_3$. The only CO-containing product is $\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$, 1995 vs, 1985 vs.

Figure 4. Infrared spectral changes in solution during the irradiation of $\text{Si}-\text{SiCo}(\text{CO})_4$, $\text{Si} = \text{Al}_2\text{O}_3$ in the presence of HSiEt_3 . The only detectable photoproduct in solution is $\text{Et}_3\text{SiCo}(\text{CO})_4$, 2027, 1996, 1991 sh cm^{-1} .

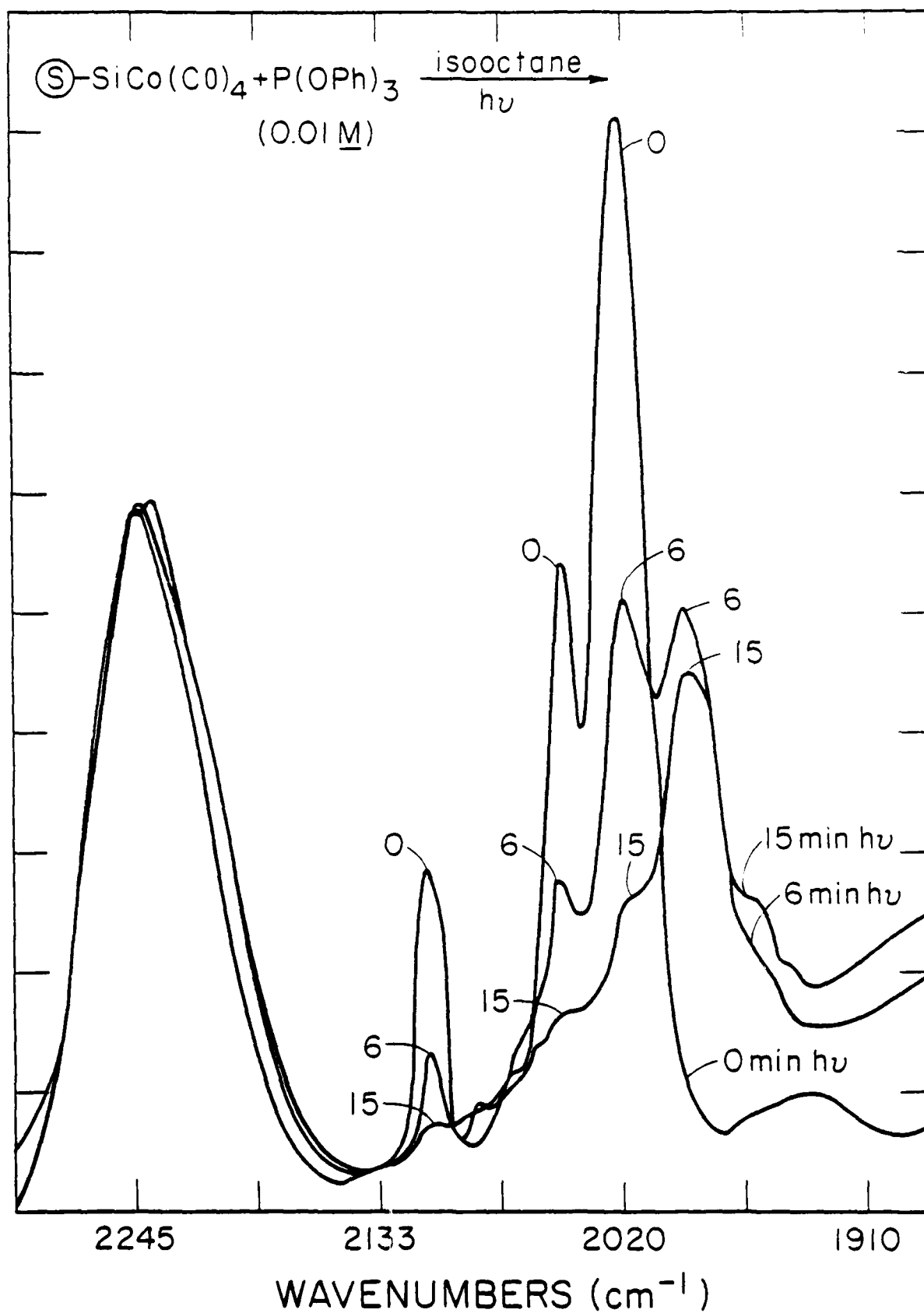
Figure 5. Infrared spectral changes of a derivatized Al_2O_3 surface accompanying irradiation in the presence of HSiEt_3 . $\text{SiCo}(\text{CO})_4$ (2110, 2050, 2020 cm^{-1}) is removed from the surface while the SiH concentration (2250 cm^{-1}) increases.

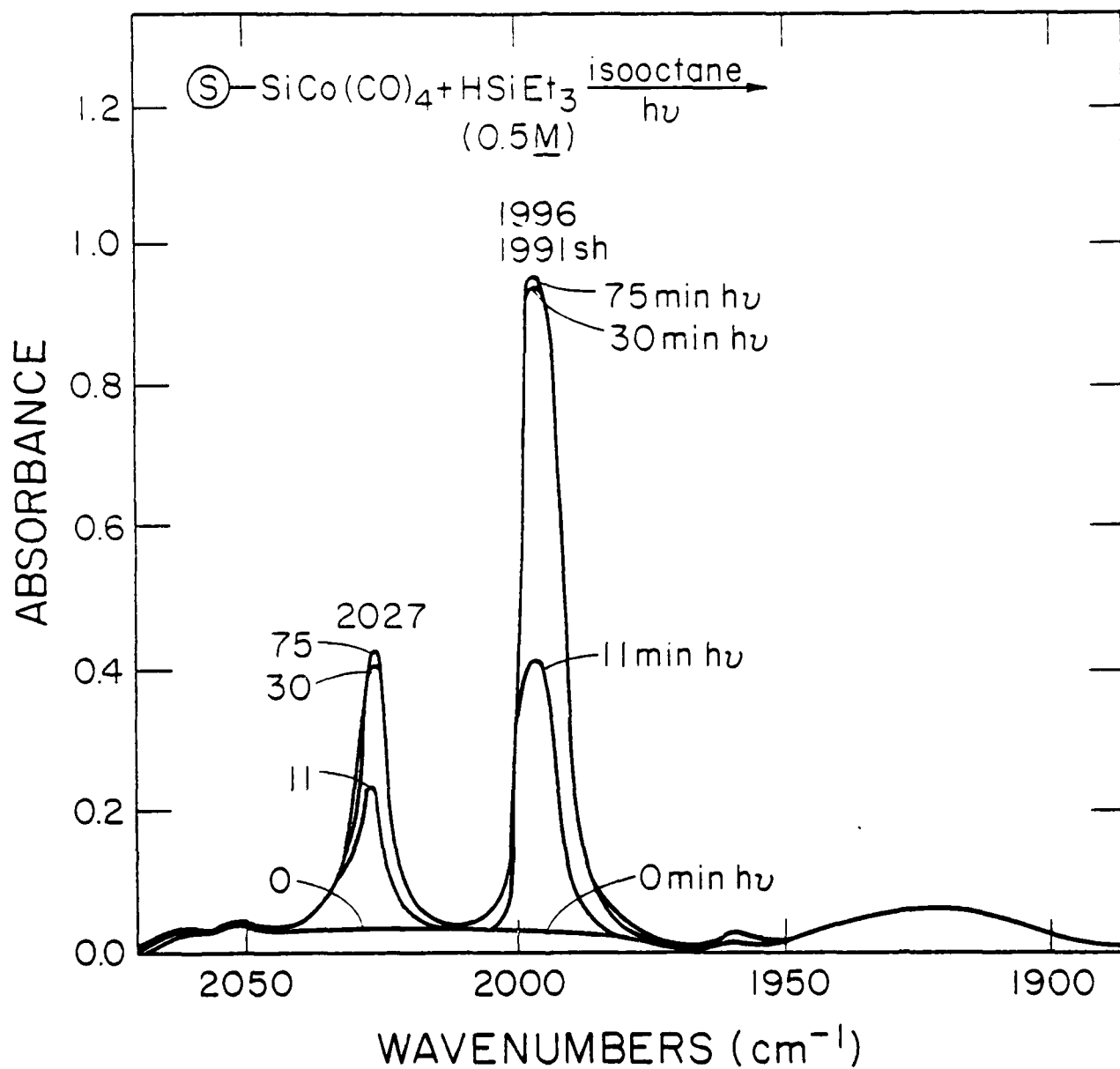
Figure 6. Infrared spectral changes in solution during the irradiation of a derivatized alumina surface in the presence of 1-pentene/ HSiEt_3 . The solution products are the same as those observed when homogeneous $\text{Et}_3\text{SiCo}(\text{CO})_4$ (photochemical) or $\text{Co}_2(\text{CO})_8$ (thermal) is used as the cobalt source. The bands at 2025, 1995, 1991 sh are due to $\text{Et}_3\text{SiCo}(\text{CO})_4$.

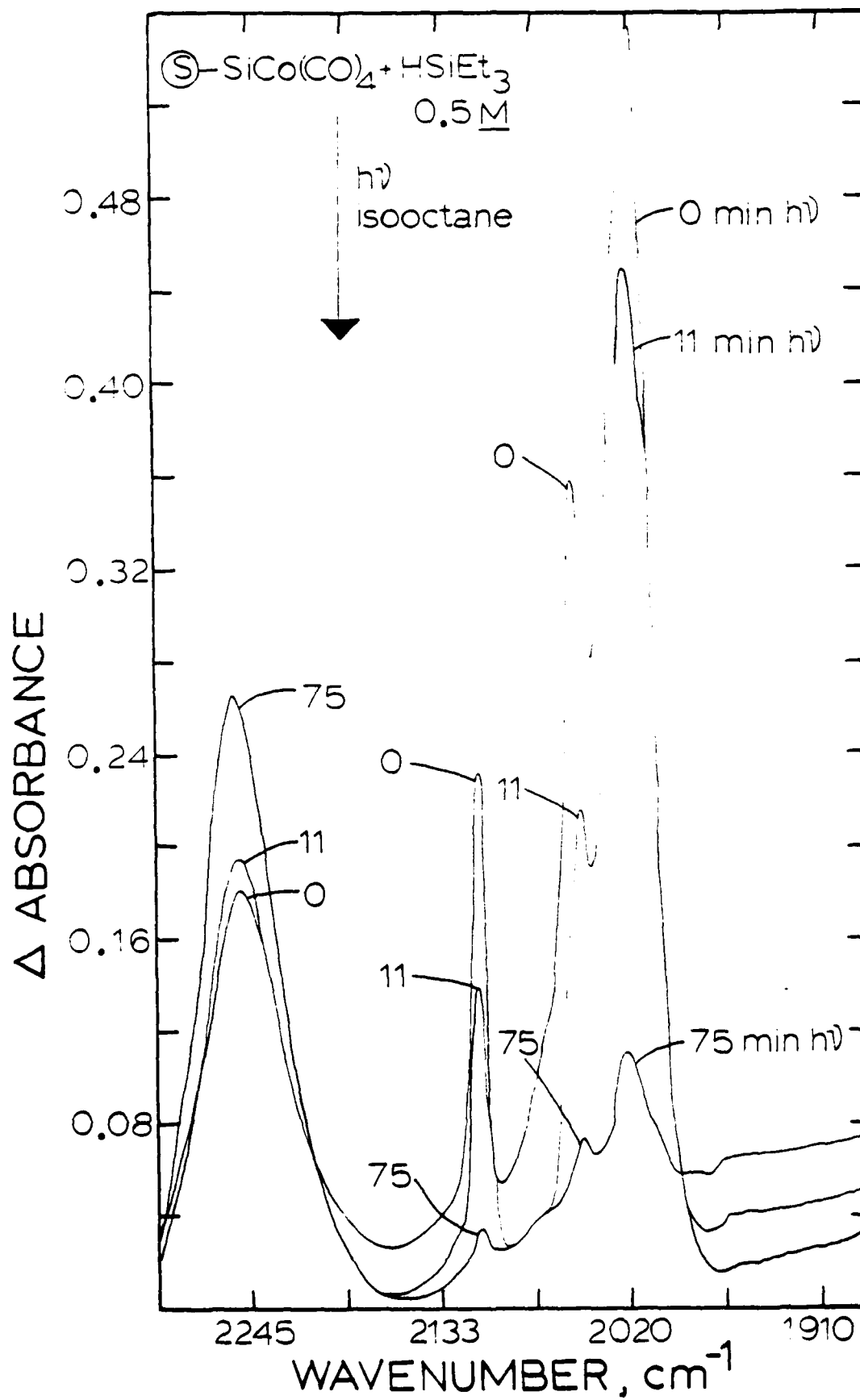


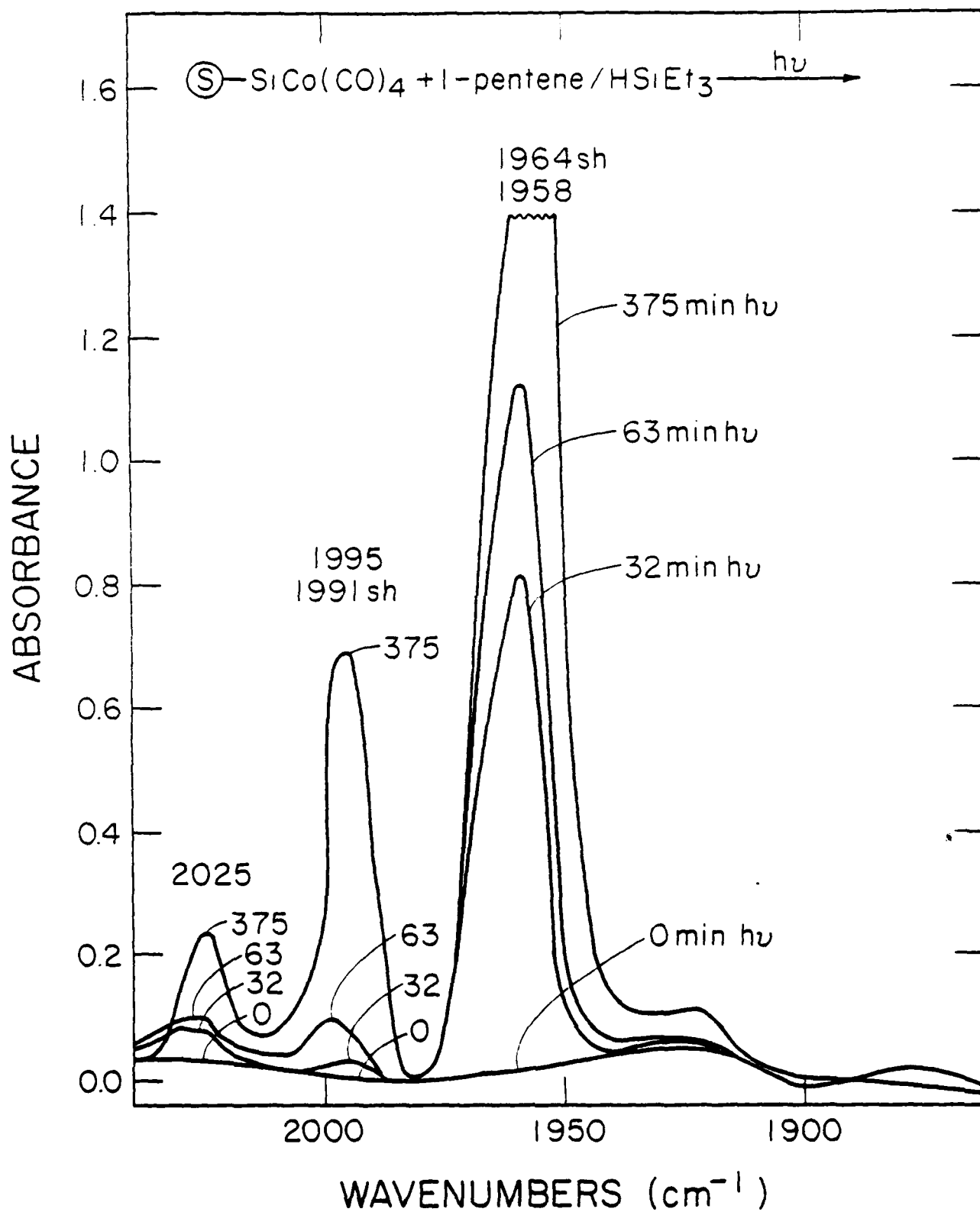


ABSORBANCE (ARBITRARY UNITS)









TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Dr. S. B. Sandoz 715 Broadway New York, New York 10005	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. S. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOE (STOR) 600 F Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

TECHNICAL REPORT DISTRIBUTION LIST, 1954

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1	Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1	Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. C. A. Heller Naval Weapons Center Code 6039 China Lake, California 93555	1	Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1	Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059	1
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1	Dr. George E. Walraffen Department of Chemistry Howard University Washington, DC 20059	1
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		

DATE
FILMED
-8